

# Occurrence of Technical Polybrominated Diphenyl Ether Mixtures in Polish Indoor Environments

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## Introduction.

In recent years polybrominated diphenyl ethers (PBDEs) have emerged as a subject of great concern, because of their increasing levels in humans, ubiquity in all environmental compartments, especially indoors, and endocrine disruptor properties (Darnerud. 2003). PBDEs have been used as flame retardant additives in a variety of plastic consumer products over the past two decades. In practice, only a few of theoretical 209 PBDE congeners are employed in the commercial BDE formulations, which are named on the basis of average bromination level – penta-, octa-, and decaBDE, respectively. The Penta mixture contains mainly BDE 47, 99, 100 with smaller contributions from BDE 28, 153 and 154; the Octa mixture contains BDE 153, 154, 183 while the Deca mixture consists mainly of BDE 209 (LaGuardia et al. 2006). The Penta mixture was used as a flame retardant for polyurethane foams in carpet underlays, vehicle interiors, furniture and beddings. However, this mixture was sometimes also used in computer circuit boards until the mid-1990s. The Octa mixture was added primarily to thermoplastics such as high impact polystyrene. The Deca mixture is used in plastic housings for electrical goods such as TVs and computers, as well as in textiles (Alaee et al. 2003). The highest PBDE levels were detected in indoor samples, namely in dust, at concentrations which were often 50-fold higher than those reported for the outdoors. This finding suggests their sources to be household products and materials (Rudel et al. 2003). PBDEs can accumulate in dust from various pathways, including vaporizing from products, transport of soil particles and aerosols from the outdoor to the indoor environment.

The occurrence of PBDEs in Poland have not been studied until very recently. There are only scarce information about levels of PBDEs in humans (Jaraczewska et al. 2006), leachate from landfills (Czerwiński et al. 2007) and household dust (Staszowska et al. 2008). Under Polish conditions, PBDEs have been never produced and there is no production currently. Hence, the only sources of these compounds in the indoors may be emission from finished imported products.

The aim of this study was to monitor and compare the levels and distribution of selected PBDE congeners commonly used in technical pentaBDE and octaBDE mixtures (BDE 28, 47, 99, 100, 138, 153, 183) present in dust in a variety of different indoor environments.

## Materials and Methods.

### *Sample collection*

A total of 30 indoor dust samples were collected from residential homes (n=20), offices (n=6), computer repair facilities (n=2), and shops with electronic devices (n=2), in different districts within the

Lublin area during January to May 2009. Lublin is a city of ca. 400 thousand inhabitants, situated in South-Eastern Poland. Dust was collected from the dust bag of the vacuum cleaners. Then, samples were passed through a 125µm stainless sieve to obtain a suitable degree of homogeneity.

### Chemicals

All chemicals used for PBDE analysis were of high purity. Toluene and dichloromethane (Ultra-Resi Analysed) were purchased from T.J. Baker (Germany). PBDE analytical mixture standards series BDE-CVS-F containing BDE 28, 47, 85, 99, 100, 153, 154, 183 congeners, as well as mass labeled (<sup>13</sup>C) PBDE recovery solution BDE-MFX containing BDE 77L and 138L were obtained from Wellington Laboratories (Ontario, Canada). Additional standard solutions of native PBDE containing BDE 28, 47, 85, 99, 100, 153, 183 congeners were obtained from Wellington Laboratories and from AccuStandards (mixture M-527 BDE).

### Analysis of PBDEs

The dust was extracted with toluene in a Soxhlet apparatus for 16 hours in a dark room. The extract was evaporated under a nitrogen stream and then the solvent was changed to dichloromethane. Further purification was performed using size exclusion chromatography (SEC) (Brezee 1525, Waters). Quantification of target BDE congeners was done using the Trace Ultra – Polaris Q GC-MS system. Parameters of the system are presented in Table 1.

Table 1. The operating conditions of GC/MS system.

| GC TRACE ULTRA                |  |
|-------------------------------|--|
| Injector                      | PTV (splitless mode) @ 320°C   |
| Capillary column              | RTx Dioxin (Restek) 60m x 0.25mm d <sub>i</sub> =0.18µm  |
| Oven temperature programming  | 85°C (0.5 min hold) ramp 15°/min to 210°C then ramp 5°/min to 320°C, 20 min hold   |
| Carrier gas                   | He (99,9996%) @ 40 cm/s  |
| MS POLARIS Q                  |  |
| The ion source temperature    | 250°C  |
| The transfer line temperature | 275°C  |
| Scanning mode I: Full Scan    | 50.0 - 850.0 amu   |
| Collision gas                 | He (99,9996%) @ 2 ml/min   |
| Scanning mode II              | SIM: quantitation ion and (qualifiers)<br>Tri-BDE (28) 406 408 (246, 248)<br>Te-BDE (47) 486 (484, 488, 326)<br>Pe-BDE ( 99, 100) 564 (566, 406, 404)<br>Hx-BDE (138, 153, 154) 643 (645, 484, 482, 186)<br>Hp-BDE (183) 723 (725, 562, 564) |

## Results and Discussion.

Congener distribution and PBDE concentration data for all sampling places in this study are summarized in Table 2. PBDE concentrations which we found were higher than previously reported by us for smaller group of Polish indoor sets ( $n=7$ ) which we examined in 2007 (Staszowska et al.2008).

Table 2. Concentrations of PBDE congeners [ $\text{ng g}^{-1}$  dust] measured in indoor dust samples.

| sampling place             | number of samples | tetraBDE |      |      |     | pentaBDE |     |      |      | hexaBDE |      |
|----------------------------|-------------------|----------|------|------|-----|----------|-----|------|------|---------|------|
|                            |                   | 28       |      | 47   |     | 99       |     | 100  |      | 153     |      |
|                            |                   | min      | max  | min  | max | min      | max | min  | max  | min     | max  |
| homes                      | $n=20$            | <dl      | 8.7  | 5.1  | 96  | <dl      | 74  | <dl  | 59.7 | <dl     | 21.4 |
| offices                    | $n=6$             | 2.4      | 29.4 | 7.4  | 111 | 5.8      | 49  | 5.1  | 33   | 6.3     | 24.7 |
| computer repair facilities | $n=2$             | 25.7     | 41.3 | 18.7 | 544 | 7.1      | 179 | 19.2 | 155  | 5.9     | 46   |
| shops                      | $n=2$             | 32.3     | 27.6 | 14.6 | 96  | 6.2      | 75  | 5.4  | 76.9 | 6.6     | 34.4 |

In most samples, congeners of the two commercial PBDE mixtures have been detected with the biggest contribution of pentaBDE one. The highest concentrations have been measured for BDE 47, 100, 99, 153 and 28, respectively. The most contaminated by PBDE indoor environments were computer repair facilities and shops with electrical devices. Moreover, obtained in our study PBDE concentrations in household and office dust samples were lower than values reported in the literature (Sjödén et al. 2008; Takigami et al., 2009; Toms et al. 2009) or similar (Gevao et al.2006; Tan et al. 2007). Differences in PBDE concentrations between our study and other studies may reflect mainly differences on the scale of PBDEs usage. In Poland, PBDEs are not produced and not so widely distributed as inorganic flame retardants. Large amounts of electronic appliances are, however, imported from countries in which PBDEs are added to polymers. In turn, the differences between PBDE levels in household dust could be related to the differences in point sources in the indoor environment (e.g. EE appliances, textiles).

The prevalence of lower brominated PBDE congeners in collected dust samples may results from DecaBDE photodegradation as well.

## Conclusions.

Despite never having produced in Poland, congeners of penta- and octaBDE commercial mixtures, have been found to occur ubiquitously in number of Polish indoor environments. Levels of target analytes was substantially lower than those reported in literature. Further investigations are needed to estimate the exposure for Poles.

**Acknowledgement.**

The authors would like to thank Mr. Jacek Czerwiński and Mr. Michał Kwiatkowski, staff of the Environmental Analysis Laboratory at the Faculty of Environmental Engineering, Lublin University of Technology for their cooperation during analytical part of study. This research was funded by the Polish Ministry of Higher Education, grant nr PB NN 52341835.

**References.**

- Alaee M., Arias P., Sjödin A., Bergman A. 2003. *Environ Int* 29:683.
- Czerwiński J., Dudzińska M.R., Staszowska A., Rut B. 2007. *Organohalogen Comp* 69:2720.
- Darnerud P.O. 2003. *Environ Int* 29:841.
- Gevao B., Al-Bahloul M., Al-Ghadban A.N., Al-Omair A., Ali L., Zafar J., Helaleh M. 2006. *Chemosphere* 64:603.
- Jaraczewska K., Lulek J., Covaci A., Voorspoels S., Kaluba-Skotarczak A., Drews K., Schepens P., 2006. *Sci Total Environ* 372:20.
- LaGuardia M.J., Hale R., Harvey E. 2006. *Environ Sci Technol* 40:6247.
- Rudel R.A., Camann D.E., Spengler J.D., Korn L.R., Brody J.G., 2003. *Environ Sci Technol* 37: 4543.
- Sjödin A., Päpke O., McGahree E., Focant J.F., Jones R.S., Pless-Muloli T., Leontiew Toms L.M., Hermann T., Müller J., Needham L.L., Patterson Jr D.G. 2008. *Chemosphere* 73:S131.
- Staszowska A., Połednik B., Dudzińska M.R., Czerwiński J. 2008. *Archives Environ Prot* 34:239.
- Takigami H., Suzuki G., Hirai Y., Sakai S. 2009. *Chemosphere* 76:270.
- Tan J., Cheng S.M., Loganath A., Chong Y.S., Obbard J.P. 2007. *Chemosphere* 66:985.
- Toms L.M.L., Bartkow M.E., Symons R., Paepke O., Mueller J.F. 2009. *Chemosphere* 76:173.